Midterm: Lecture, 19, 21, 26th

① Review 28th
Send midterm on 28th
Th 28th – Wed 3rd

Midterm 1-2 class length
midterms

② HW next week

③ Computation

Outline:

Before: microcanonical & canonical ensembles, entropy & free energy

Currently: can't solve most problems, computers solve, by statistical sampling

Today MD

Next: approximate solutions [gasses & liquids]

Later: Phase transitions
Dynamics, Non Eq

Canonical Sampling $\quad P(q,p) \propto e^{-\beta \mathcal{H}(p,q)}$

But, MD gives microcanonical distribut.

First: Integration algorithm

$$\frac{dq}{dt} = \frac{\partial \mathcal{H}}{\partial p} \leftarrow \text{velocity} \qquad \frac{dp}{dt} = -\frac{\partial \mathcal{H}}{\partial q} \leftarrow \text{force}$$

$$q(t+\Delta t) = q(t) + \Delta t \frac{dq}{dt}$$

small Δt approx

$$p(t+\Delta t) = p(t) + \Delta t \frac{dp}{dt}$$

Verlet, Velocity verlet algorithms

Taylor expansions of position

① $$q(t+\Delta t) = q(t) + \Delta t \underbrace{\frac{dq}{dt}\Big|_t}_{v(t)} + \frac{\Delta t^2}{2} \underbrace{\frac{d^2 q}{dt^2}\Big|_t}_{\substack{a(t) \\ = F(t)/m}} + \cdots$$

$$q(t+\Delta t) = q(t) + \Delta t\, v(t) + \frac{\Delta t^2}{2} F(t)/m$$

② $$q(t-\Delta t) = q(t) - \Delta t\, v(t) + \frac{\Delta t^2}{2} F(t)/m$$

add eqns $$q(t+\Delta t) + q(t-\Delta t)$$

$$= 2q(t) + \Delta t^2 F(t)/m$$

$$q(t+\Delta t) + q(t-\Delta t)$$

[Verlet 1967]

$$= 2q(t) + \Delta t^2 F(t)/m$$

$$q(t+\Delta t) = 2q(t) - q(t-\Delta t) + \Delta t^2 \frac{F(t)}{m}$$

store q, $q(t-\Delta t)$

calculate force every time

[Bruce Berne, Rahman lecture]

$$v(t) = \frac{q(t+\Delta t) - q(t-\Delta t)}{2\Delta t}$$

Get another scheme by, going back in time

$q(t+\Delta t) \to q(t)$

$$\cancel{q(t)} \approx \cancel{q(t+\Delta t)} - \Delta t \, v(t+\Delta t) + \frac{\Delta t^2}{2}\frac{F(t+\Delta t)}{m}$$

$-$

① $$\cancel{q(t+\Delta t)} \approx \cancel{q(t)} + \Delta t \, v(t) + \frac{\Delta t^2}{2}\frac{F(t)}{m}$$

add one from other

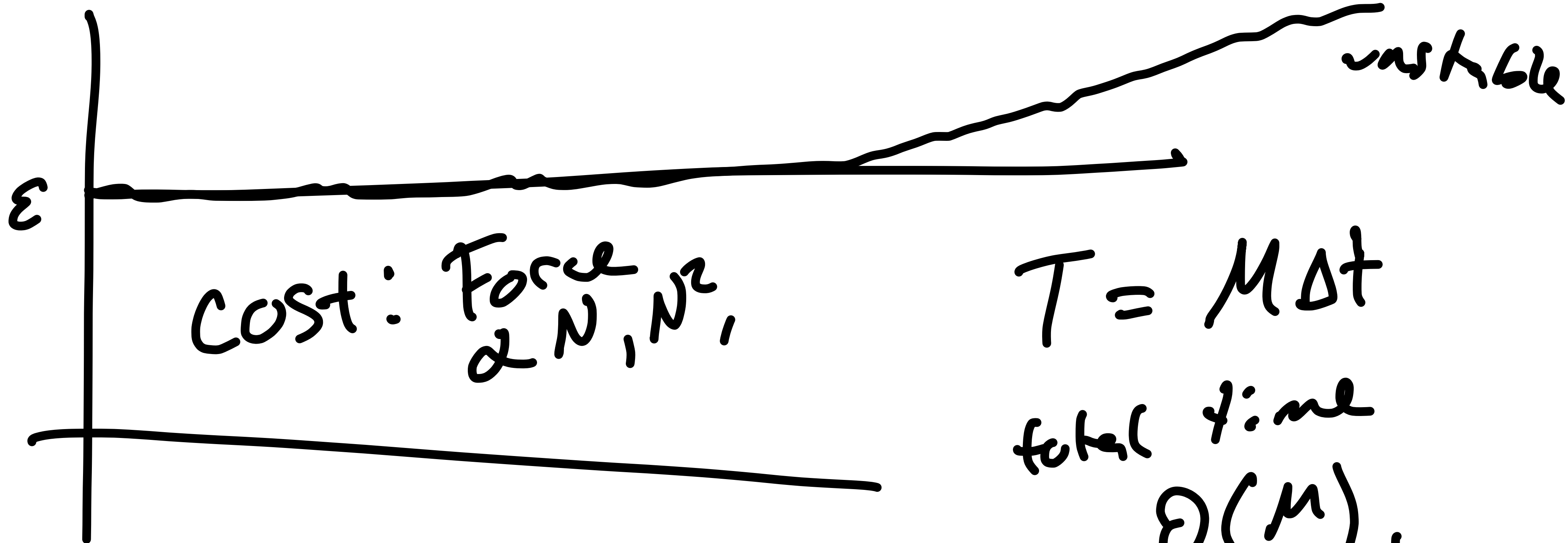
② $$v(t+\Delta t) = v(t) + \frac{1}{2}\frac{\Delta t}{m}\left[F(t) + F(t+\Delta t)\right]$$

alternate 1 & 2

store $q(t), p(t), F(t)$

Know: $q(0), v(0)$

[Velocity Verlet algorithm]



cost: Force $\propto N, N^2,$

$T = M \Delta t$

total time

$\mathcal{O}(M)$

$\propto M \cdot N^d$

stability $\propto \Delta t^n$

[see furthermore

Formally $A(t) = e^{i\mathcal{L}t} A(0)$

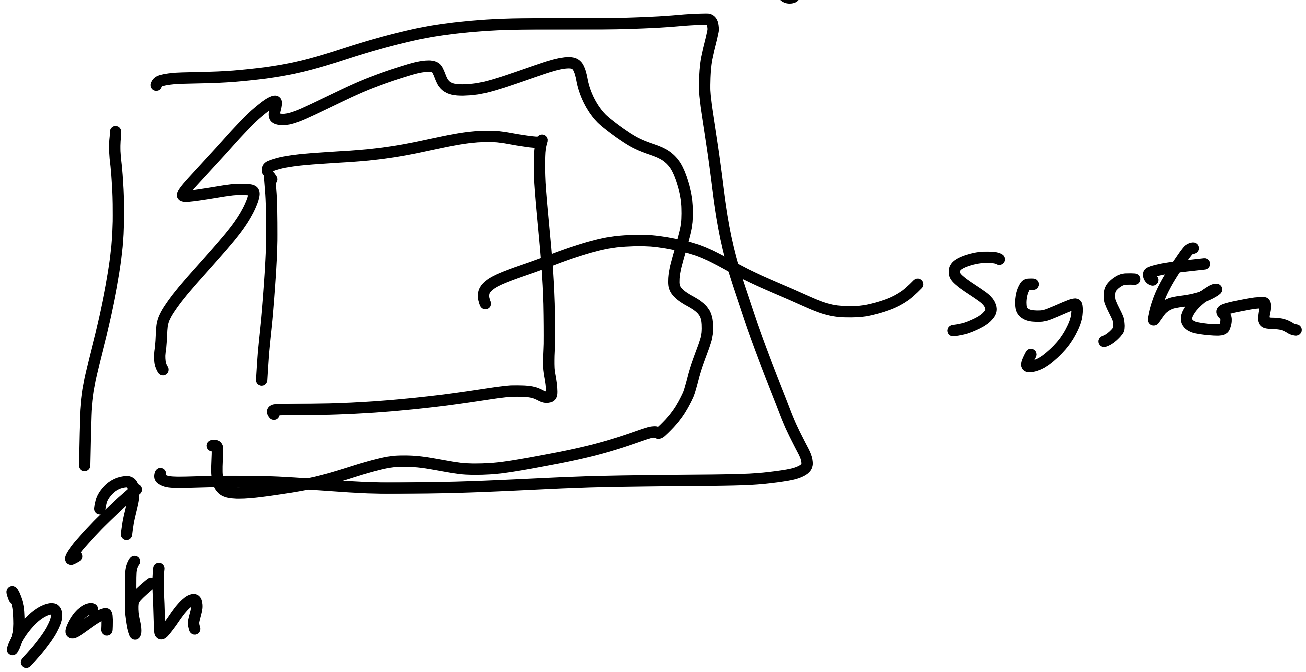
$A = \{q, p\}$

trotter factorization →

velocity verlet

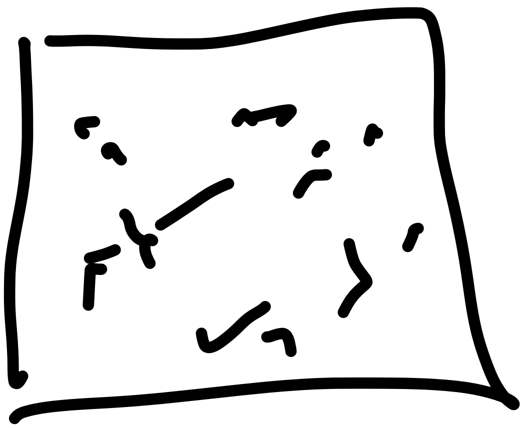
That was microcanonical

How do we get canonical sampling



3 early approaches - not accurate

① temperature rescaling



calculate temperature:

$$P(v) = e^{-\beta \frac{1}{2} m v^2} \Big/ \sqrt{2\pi m k_B T}$$

$$\langle v^2 \rangle = \frac{k_B T}{m}$$

$$\langle KE \rangle = \langle \tfrac{1}{2} m v^2 \rangle = \frac{k_B T}{2}$$

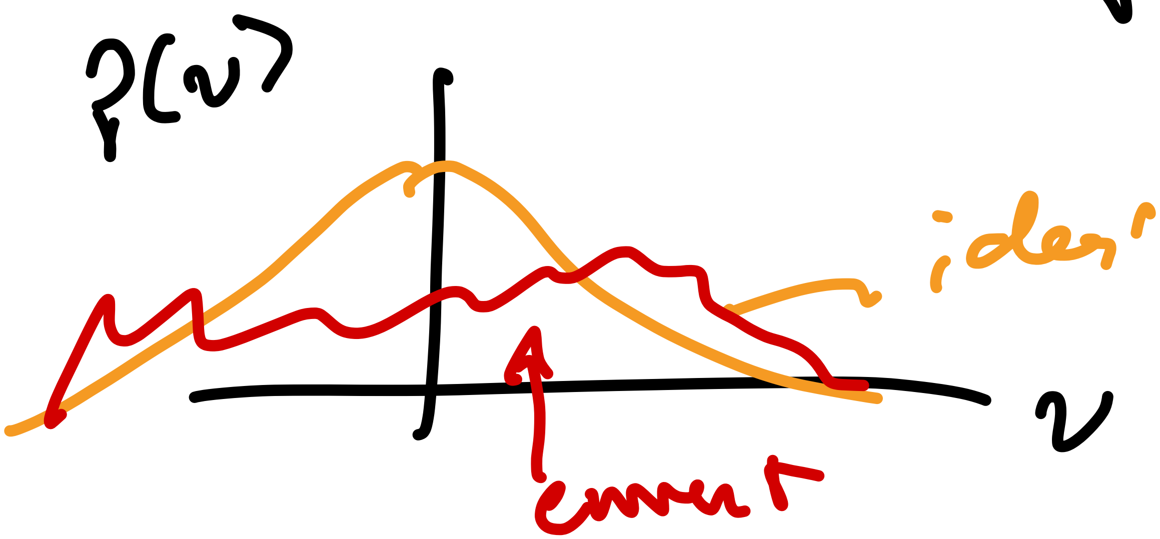
$$\left\langle \sum_{i=1}^{3N} \tfrac{1}{2} m_i v_i^2 \right\rangle = \frac{3}{2} N k_B T$$

avgKE

$$k_B T_{current} = 2 \left\langle \frac{1}{3N} \sum_{i=1}^{3N} \tfrac{1}{2} m_i v_i^2 \right\rangle$$

$$\frac{k_B T_{current}}{k_B T_{ideal}} = \frac{m v^2(t)}{m v^2_{ideal}(t)}$$

$$v_{ideal} = v(t) \cdot \sqrt{\frac{T_{ideal}}{T_{current}}}$$



only fixes mean squared velo.

kind of preserves inertia

② Resampling

Reset all velocities from

$$p(v) = e^{-\beta \frac{1}{2} m v^2} / \sqrt{2\pi k_B T m}$$

Completely loses inertia

③ Anderson thermostat

randomly pick a particle with (some)

rate ν, resample velocity

choose random number $r < \nu \Delta t$, resample

Better ideas:

① Langevin dynamics
[later, non eq]
adding random forces

② Extendended ensmble
Nosé [1983, 84]
add an extra "fake particle"
keep track of KE, if too big
or small, velocities get rescaled

$$\mathcal{H}_N = \sum_{i=1}^{dN} \frac{\tilde{p}_i^2}{2ms^2} + U(q) + \underbrace{\frac{p_s^2}{2Q}}_{\text{KE of } s} + \underbrace{g k_B T \ln(s)}_{U(s)}$$

$p_i = \tilde{p}/s$

Q "mass of s"
controlls how fast
rescaling happens

EOM:

$dN+1$ positions & $dN+1$ momenta

$\{q_i, \tilde{p}_i, s, p_s\} \leftarrow 2dN+2$

$$\mathcal{H}_N = \sum_{i=1}^{dN} \frac{\tilde{p}_i^2}{2ms^2} + U(q) + \underbrace{\frac{p_s^2}{2Q}} + \underbrace{g k_B T \ln(s)}$$

$$\dot{q}_i = \frac{\partial \mathcal{H}}{\partial \tilde{p}_i} = \frac{\tilde{p}_i}{m_i s^2}$$

$$\dot{\tilde{p}}_i = -\frac{\partial \mathcal{H}}{\partial q_i} = -\frac{\partial U}{\partial q_i} = F_i$$

$$\dot{s} = \frac{\partial \mathcal{H}}{\partial p_s} = p_s / Q$$ "velocity of s"

$$\dot{p}_s = -\frac{\partial \mathcal{H}}{\partial s} = \sum \frac{\tilde{p}_i^2}{2ms^3} - \frac{g k_B T}{s}$$

$$= \frac{1}{s}\left[\sum \tilde{p}_i^2 / ms^2 - g k_B T\right]$$

g turns out be $(dN+1)$

$$\frac{dp_s}{dt} = \frac{1}{s}\left[\sum \tilde{p}_i^2/ms^2 - g k_B T\right]$$

$$= \frac{1}{s}\left[2K\varepsilon - (dN+1)k_B T\right]$$

[See Book]

$$\Omega(N,V,\varepsilon) = \int dq^{dN} \int dp^{dN} \int ds \int dp_s$$

$$\delta\left(\mathcal{H}(\tilde{p},q) + \frac{p_s^2}{2Q} + g k_B T \ln s\right)$$

$$\propto \quad e^{-\beta \mathcal{H}_{real}(p,q)} \quad \text{if } g = dN+1$$